

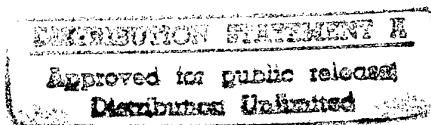
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Date: April 5, 1993

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Subject: Annual report regarding the project "Ambient and Subambient Temperature Polymeric Electrolytes"
(Contract SPC-92-4007; F61708-92-W0306)

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Within this project studies were carried out on three basic systems:

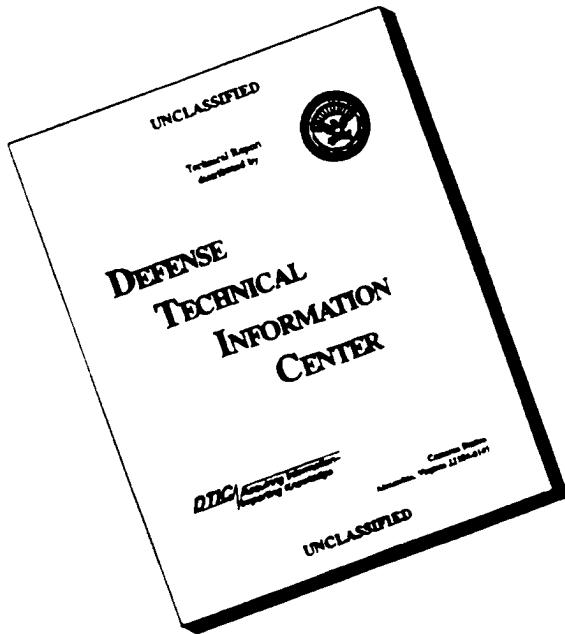
1. Polymer gel electrolytes based on glycidyl methacrylate homopolymer and copolymers.
2. Electrolytes with immobilized anions based on styrene - maleic anhydride copolymers.
3. Poly(ethylene oxide) blends with methyl methacrylate / acrylonitrile copolymers.

1. Polymer gel electrolytes based on glycidyl methacrylate homopolymer and copolymers.

A polymer gel can be prepared from macromolecules capable of forming three-dimensional networks around the solvent. One of the possibilities is the use of linear polymers such as acrylonitrile or polyvinylformal, in which strong interactions occur between the crystalline regions within the macromolecular chain [1-3]. However, crosslinked polymers are used for this purpose much more often. This last strategy involves the radiation crosslinking of linear polymers [mainly poly(ethylene oxide); (PEO)] or radiation initiated polymerization of bi- and trifunctional acrylic type monomers in the presence of appropriate organic solvents [4-6]. The obtaining of systems containing 70-80% of the solvent of good dimensional stability seems to be the key problem. These type of electrolytes

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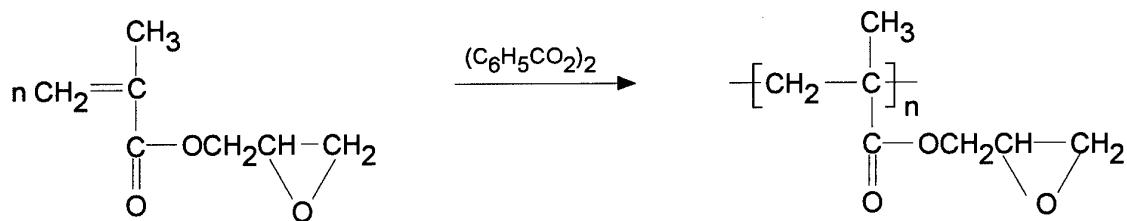
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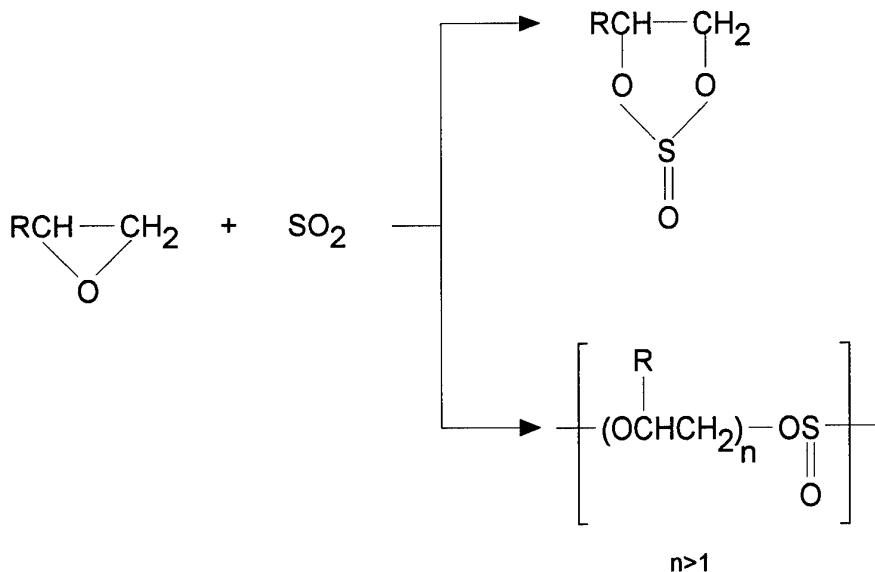
may exhibit conductivity in the range of 10^{-4} - 10^{-3} S/cm at ambient temperature.

In our studies we decided to obtain gel electrolytes in two-step polymerizations. In the first step a linear polymer solution would be obtained, which then would be subjected to crosslinking resulting from chemical processes.

In one of the systems studied, glycidyl methacrylate (GMA) was the main monomer. The polymerization of GMA in propylene carbonate at 70°C at a 50-80 wt% content of the solvent in the presence of 1 wt% of benzoyl peroxide as initiator is completed after about 90 minutes



The viscous solutions obtained are completely homogeneous. When the reactions are carried out in the presence of LiClO_4 (8 wt%), in systems containing 50 and 60 wt% of propylene carbonate, spontaneous crosslinking proceeds leading to the formation of homogeneous gels. The mechanism of this reaction is not determined but it is known that at elevated temperature LiClO_4 may initiate the crosslinking of compounds with a high epoxide groups concentration [7]. However, if the solvent constitutes 70 or more wt% of the reaction mixture, crosslinking does not proceed even when heating the sample at 70°C for 100 h. For this reason we decided to introduce to the system also compounds which may initiate the cationic polymerization of epoxide groups. SO_2 was used first. In the presence of this compound the crosslinking can be carried out at 50°C during 12-24 hrs depending on the monomer concentration, and the gels obtained are homogeneous and transparent. The elemental analysis of the product washed off from the solvent and LiClO_4 indicates a 43 mol. % content of SO_2 in it. From the reaction of oxiranes with SO_2 it is known that they lead to the formation of cyclic sulfites and linear poly(ether-sulfite)s.



In the IR spectrum of the polymer obtained bands characteristic for cyclic sulfites mainly occur ($\nu_{\text{S=O}} \sim 1200$; $\nu_{\text{C-O}} \sim 1005, 910$; $\nu_{\text{S-O}} \sim 740$; $\delta_{\text{CH}_2} \sim 1465 \text{ cm}^{-1}$).

Studies on the model reaction using glycidyl acetate as the substrate of poly(glycidyl methacrylate) indicated that under analogous conditions about 90% of epoxide groups take place in the cyclization. However, the SO_2 content in linear products does not exceed 10 mol. % ($n > 10$). When accepting that also under the conditions of gelling, SO_2 is consumed nearly exclusively for the formation of cyclic products then it can be expected that not more than 20% of epoxide groups are involved in crosslinking.

Gels containing up to 80 wt% of propylene carbonate are homogeneous and they can be easily pressed to thin films, simultaneously maintaining dimensional stability under the conductivity measurement conditions. In Table 1 are presented the conductivities of this type of electrolytes at 25 and 50°C. As can be seen, at a constant concentration of the salt the conductivity clearly increases with an increase of the solvent content. For a gel containing 80 wt% of propylene carbonate the average conductivity is $1.6 \cdot 10^{-3} \text{ S/cm}$ at ambient temperature (three independent syntheses were carried out resulting in the values: $1.5 \cdot 10^{-3}$, $1.6 \cdot 10^{-3}$ and $1.7 \cdot 10^{-3} \text{ S/cm}$, respectively). The activation energy calculated according to the VTF method is very low and equals 0.119 eV. For a sample containing 5 wt% of LiClO_4 conductivity studies were also carried out at 0 and -78 °C; the conductivity values obtained were equal to $3.4 \cdot 10^{-4}$ and $3.3 \cdot 10^{-7} \text{ S/cm}$, respectively. At a 70 wt% propylene carbonate content in the gel, $\sigma_{\text{rt}} = 2.6 \cdot 10^{-4} \text{ S/cm}$ and the activation energy = 0.209 eV. When decreasing the

salt concentration to ~ 6 wt% the salt conductivity changes are minimal; however, the conductivity decreases considerably at a concentration of about 4 wt%.

We found that systems with LiCF₃SO₃ exhibit a lower conductivity. In view of the recent work of Prud'homme et al. [8] it seems that ion pairing takes place to a lesser extent in the LiClO₄ electrolytes, which results from the higher polarization of the "soft" CF₃SO₃⁻ anion in comparison to the "hard" ClO₄⁻ anion. We found that homogeneous gels can be prepared also using cyclic sulfites as solvents: propylene sulfite (1,2,3-dioxathiolane-4-methyl-2-oxide) and 3-chloropropylene sulfite (1,2,3-dioxathiolane-4-chloromethyl-2-oxide). Gels with propylene sulfite exhibit similar conductivities to those of gels with propylene carbonate. However, gels with 3-chloropropylene sulfite exhibit conductivities of an order of magnitude lower.

From the studies carried out by us on the conductivity of LiClO₄ in solutions of ethylene sulfite, propylene sulfite, and 3-chloropropylene sulfite it appears that the conductivity decreases with an increase of the molecular weight of the sulfite used. In Fig. 1 are presented the changes of conductivity vs salt concentration (up to saturated solutions) at 20°C. In the case of ethylene sulfite the maximal concentration is ~1.3 mol/kg, and $\sigma \sim 3.0 \cdot 10^{-2}$ S/cm, for propylene sulfite 1.55 mol/kg and $2.2 \cdot 10^{-2}$ S/cm, respectively and in the case of 3-chloropropylene sulfite 1.2 mol/kg and $3.6 \cdot 10^{-3}$ S/cm, respectively. The activation energies determined for the 20-60°C range were equal to 0.05, 0.103 and 0.198 eV for ethylene, propylene and 3-chloropropylene sulfite, respectively. It seems that the reason for the decrease in conductivity with an increase of the sulfite molecular weight is the rising viscosity of solution, and hence a decrease in ion mobility.

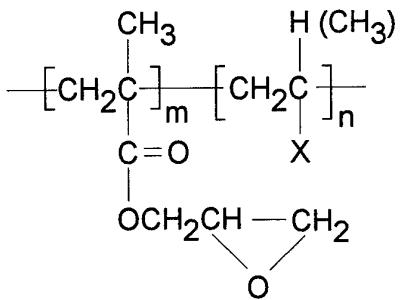
Unfortunately ethylene sulfite, which assures the highest conductivity, appeared to be too volatile to form stable gels and even at room temperature slow evaporation of this solvent from the samples occurred. (Perhaps in the next stage we shall try to use it in a mixture with other solvents; we are also considering the possibility of using other sulfites, since we evaluated a simple and productive method of their synthesis from epoxides and SO₂).

In the next stage of studies equimolar copolymers of glycidyl methacrylate with acrylonitrile, methyl acrylate, acrylamide and styrene were obtained in propylene carbonate in the presence of LiClO₄. These copolymers were subjected to crosslinking by means of SO₂. No network was obtained in the system with styrene (probably due to the large contribution of

the alternating structure, lack of glycidyl methacrylate segments and too large distance between the epoxide groups capable of crosslinking). In the other systems gels were obtained of good mechanical properties and high conductivity (Table 1). The highest values of conductivity at 25°C were obtained for copolymers with acrylamide and acrylonitrile: $3.3 \cdot 10^{-3}$ and $3.8 \cdot 10^{-3}$ S/cm, respectively (these are one of the highest values obtained for gel electrolytes). Thus, it can be assumed that the presence of a strongly polar C≡N or [C(O)NH₂] group in the polymer matrix has some influence on the overall conductivity, despite that it proceeds exclusively in the liquid phase. A change in the dielectric constant of the system may be the reason for this.

Attempts to crosslink the polymers by means of BF₃·(C₂H₅)₂O (20 wt% solution in propylene carbonate) were the next stage of studies. It is known that this initiator causes a very rapid cationic polymerization of the epoxide ring. The reactions were carried out at room temperature during 5-30 minutes using 0.1 wt% of the initiator.

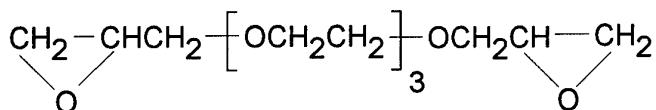
It appeared that no stable gels can be obtained by this method from GMA homopolymers. At a 60 and more wt% content of propylene carbonate the formation of a brittle powder and separation of the solvent is observed. This is probably connected with the too high crosslinking density, which results in too short network segments to successfully bound the solvent and assure elasticity of the system. IR studies of the product indicate that in these reactions all the epoxide groups are practically used up in the crosslinking. As was mentioned, in systems with SO₂ only a small part of the epoxide groups were used for the network structure, which assured an appropriate length of the linear segments between the network nodes. In this situation it appeared essential to use copolymers with other monomers to decrease the concentration of epoxide groups in the chain.



As can be seen from Table 2, in these systems also gels of conductivity above 10^{-3} S/cm at ambient temperature at 80 wt% solvent

content and above 10^{-4} S/cm at about 70 wt% solvent content. Due to the high activity of the initiator in this system, the crosslinking proceeds also in the case of polymers with styrene, which did not undergo crosslinking by means of SO_2 . It can be also noticed that it is sufficient to use about 15 mol. % of MGA to obtain stable gels, i.e. it is enough for the network nodes to occur every 5-7 monomeric units, similarly as in systems with SO_2 .

An appropriate distance between the network nodes permitting the obtaining of stable, elastic gels can be maintained also by copolymerization of the GMA homopolymer with diglycidyl compounds, in which the epoxide groups are separated from each other by a elastic segment, e.g. of the following structure:



The copolymerization proceeds in the crosslinking step. As can be seen from Table 2, this type of gels can also exhibit conductivity over 10^{-3} S/cm at 25°C .

When using $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$, gels can be obtained directly in the form of films. In Table 3 are presented a number of such films obtained and mass losses of these films at several chosen temperatures. The thermal stability of these samples up to about 60°C can be assumed as good. At elevated temperature the mass loss is slightly larger than that of materials obtained when using bi- and trifunctional methacrylates in a one-step procedure (2-3 wt% at 100°C) [5]. However the preparation of electrolytes using $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$ is experimentally difficult because of the very short reaction time

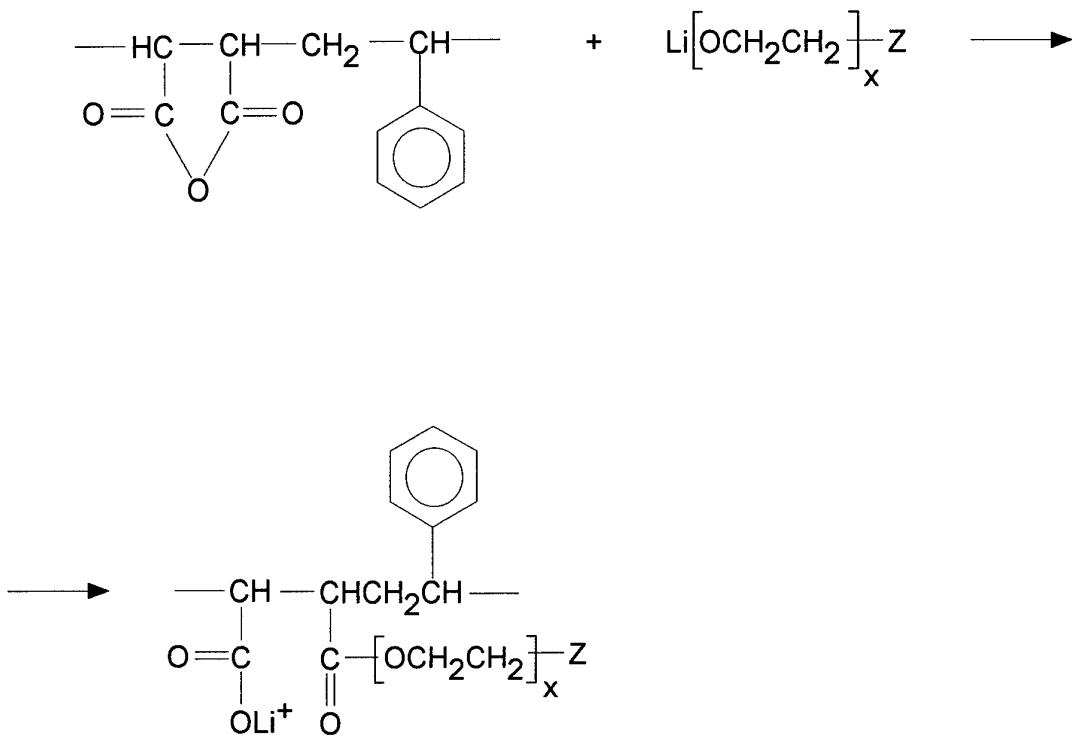
From the comparison of data for equimolar copolymers with methyl acrylate, acrylonitrile and acrylamide presented in Tables 1 and 2 it appears that the mode of crosslinking has hardly any effect on the conductivity of the gels obtained. In our opinion the method with SO_2 is more favorable, since the process can be easily controlled and the unreacted SO_2 can be easily removed from the gel by evaporation, while small amounts of BF_3 may be a harmful impurity.

By means of SO_2 we also obtained gels in a one-step copolymerization with allyl glycidyl ether ($\text{CH}_2=\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$). The conductivity has been studied of electrolytes comprising 22 wt% of the copolymer, 8 wt% of propylene carbonate, propylene sulfite and 3-chloropropylene sulfite. The following conductivity values were determined at

20°C: $1.5 \cdot 10^{-3}$, $1.6 \cdot 10^{-3}$ and $2.0 \cdot 10^{-4}$ S/cm, respectively, and the activation energies were equal to 0.119, 0.108 and 0.241 eV, respectively. This type of gels, however, undergoes pressing with great difficulty and it is difficult to obtain thin films with good mechanical properties.

2. Electrolytes with immobilized anions based on styrene - maleic anhydride copolymers.

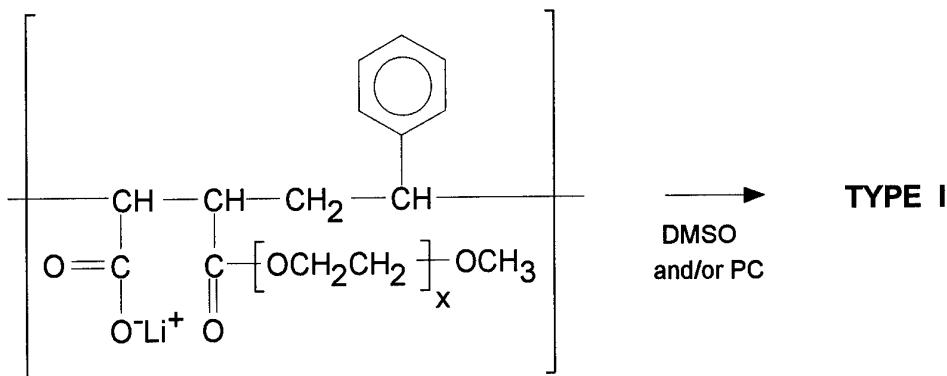
It is known that solid polymeric electrolytes with immobilized anions exhibit a much lower conductivity than that of electrolytes in which both anions and cations participate in the charge transport [9]. Moreover, the complicated method of synthesis is an additional disadvantage of a majority of these electrolytes. Previously we showed that this type of systems can be relatively easily obtained by reacting the copolymer of styrene and maleic anhydride with poly(ethylene oxide) glycol salts.



In our previous studies [10,11] the substituent Z was OH and ambient temperature conductivities for Li^+ salts varied from $8.0 \cdot 10^{-9}$ to $1.5 \cdot 10^{-5}$ S/cm depending on x (ethylene oxide side chain length). The optimum x value was equal to 4-5.

Within this work we decided to study whether there exists a possibility to increase the conductivity of these systems by permanently introducing a solvent to them. Since when using lithium electrodes the presence of alcoholic groups (OH) is not advantageous, we decided to replace it by other substituents.

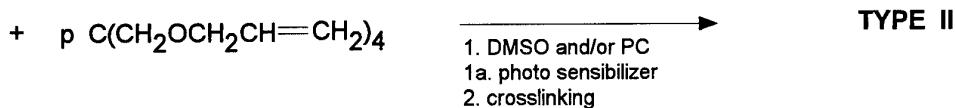
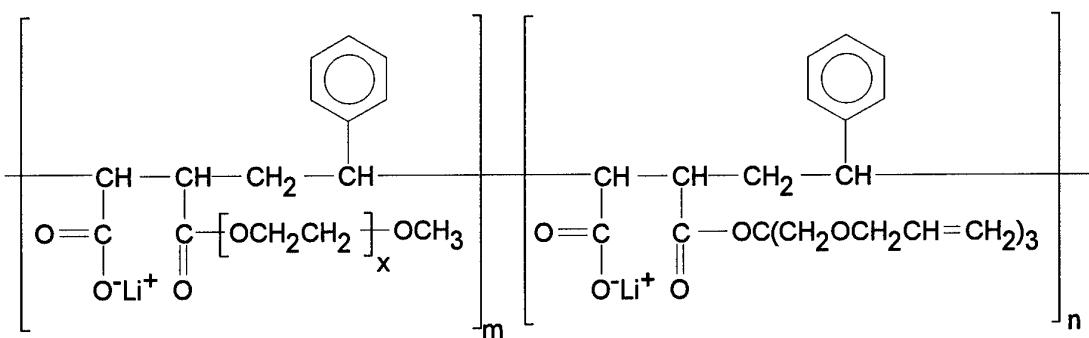
The first series of experiments was carried out for systems in which $Z = \text{OCH}_3$ (TYPE I), $x = 2, 16, 45$.



where $x = 2, 16, 45$

As can be seen from Table 4, this type of electrolytes exhibits a relatively low conductivity, below 10^{-7} S/cm at ambient temperature. This conductivity decreases with an increase in the chain length, which may result from a decrease in the Li^+ ions concentration. In the case of electrolytes of $x = 16$ it appeared possible to obtain a mechanically stable system with 20 wt% of propylene carbonate, the conductivity of which was $6.6 \cdot 10^{-5}$ S/cm at 25°C and $1.7 \cdot 10^{-4}$ S/cm at 50°C . In the case of the other systems the mechanical properties of mixtures with propylene carbonate were not satisfactory.

In order to improve the mechanical properties of these electrolytes and to obtain stable gels it was decided to introduce to the electrolyte's structure groups capable of crosslinking. Structures of two types of electrolytes obtained are presented on pages 9 and 10:



where $x = 2, 16, 45$

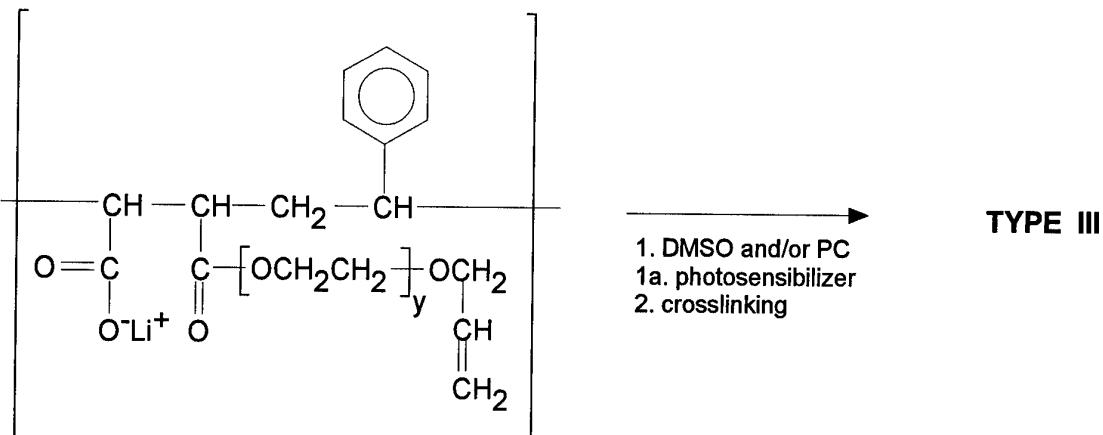
$m:n:p = 90:10:2.5$

These electrolytes were prepared in a DMSO solution, which was then removed *in vacuo* at 60°C in the presence of a photosensibilizer (or free-radical initiator). During that time crosslinking occurred and films of very good mechanical properties were obtained, in which about 8-28 wt% of DMSO was bounded permanently.

As appears from Table 4 such electrolytes exhibit conductivities in the $10^{-6}\text{-}2.4\cdot10^{-4}$ S/cm range at ambient temperature. Type III systems with relatively short ethylene oxide segments seem to be most advantageous.

Attempts have been made to additionally introduce propylene carbonate to the system and mutually evaporate both solvents. As can be seen from Table 2, such a procedure leads to an increase in conductivity to about $7\cdot10^{-4}$ S/cm at ambient temperature and above 10^{-3} S/cm at 50°C.

In Figs 2-5 are presented as an example conductivity changes vs temperature. As can be seen, a system of high conductivity is characterized by a rather low activation energy. The VTF parameters for some electrolytes are presented in Table 5.



where $y = 3, 6, 9$

For the TYPE III electrolyte of $y = 3$ containing 20 wt% of DMSO and 20 wt% of PC, investigations were carried out on its stability in the presence of a lithium electrode. We have examined this problem using a.c. impedance spectroscopy of the system comprising a gelled electrolyte sandwiched between two identical lithium metal electrodes.

The ionic conductivity of the sample studied was $8.02 \cdot 10^{-4}$ S/cm at 25 °C and $1.78 \cdot 10^{-3}$ S/cm at 50 °C giving respective values in relation to the conductivities of the corresponding system of blocking electrodes ($7.7 \cdot 10^{-4}$ S/cm and $1.9 \cdot 10^{-3}$ S/cm, respectively).

In Fig. 6 are presented impedance diagrams for a symmetrical Li PGE Li cell at 40 °C. One can easily identify two intercepts on the real axis. The first one at high frequencies may be attributed to the electrolyte resistance (R_E), and the second one at lower frequencies to the resistance of the electrode - electrolyte interface (R_i). From this figure it appears that the resistance of the interface (R_i) increases slightly with time, indicating a relatively slow (but essential) growth of a resistive layer at the interface.

Since the electrolytes were obtained under carefully controlled water-free conditions, the small passivation layer at the interface cannot be simply related to residual water and formation of an oxide layer. It seems that the effect observed results mainly from a direct reaction between the lithium anode and the electrolyte (especially the plasticizers: PC and DMSO). Considering the lithium passivation processes observed in liquid organic electrolyte systems, one cannot exclude that both plasticizers undergo partial conversion to side products in the presence of lithium, which form the

passivation layer observed. The results obtained let us suppose that the lithium electrode - PGE interface is affected by passivation phenomena similar to those observed in typical liquid organic electrolytes.

As can be seen from Table 6 this electrolyte (III D) is characterized by a small mass loss, up to ~150°C, and thus the possibility of solvent evaporation at ambient temperature is small.

The problem of preparing electrolytes of a defined composition and degree of crosslinking has not yet been considered in these systems. One of the methods applied by us was the precipitation of the polymer from the DMSO solution with an aqueous HCl solution and drying of the acidic form (H^+ is introduced instead of Li^+), and then the dissolution of the dry polymer in methanol, repeated introduction of Li^+ ions (in reaction with *n*-butyllithium), addition of a determined amount of propylene carbonate or DMSO, evaporation of methanol and finally crosslinking of the system. Such a procedure permits to control the solvent content with an accuracy of ± 3 wt%. However, it has also some inconveniences. First of all it cannot be used for the most promising samples of TYPE III, since they undergo crosslinking during drying. In order to avoid this we used mixed systems, in which unsaturated esters constituted only 30 mol. % of the polymer and the $CH_3O \cdot (CH_2CH_2O)_2$ was the remaining part. However, these products underwent crosslinking too slowly and the mechanical properties of the gels are insufficient. In the case of TYPE II samples, during isolation a tetra-functional component $[CH_2=CHCH_2OCH_2]_4C$ is eliminated from the polymer, which also decreases the degree of crosslinking and worsens the mechanical properties of the gel. However, films of conductivity of about $7 \cdot 10^{-4}$ S/cm at 20°C, $8 \cdot 10^{-5}$ at 0°C and $2 \cdot 10^{-5}$ S/cm at -55°C can be obtained by this method and such a sample has been sent to the Wright Patterson Lab, AFB, Dayton, Ohio, USA.

In our opinion these problems are of a technical nature and mainly require patient optimization of the conditions of film preparation. We hope to solve these problems during further studies. There are many possibilities of improving the mechanical properties and conductivities of these systems, eg. by additional introduction of very polar crosslinking monomers and increase of the lithium cations concentration, which is much lower in these systems than that in classic gel electrolytes.

3. Blends of PEO with methyl methacrylate / acrylonitrile copolymers.

We have proved previously that it is possible to considerably increase the ambient temperature conductivity of PEO - inorganic salts complexes by addition of different polar polymers to them [12-15]. This effect is especially distinct in the case of immiscible blends with isotactic poly(methyl methacrylate) or poly(acrylamide), which exhibit conductivity of over 10^{-5} S/cm at ambient temperature.

Within this work we studied electrolytes containing copolymers of two polar monomers: methyl methacrylate (MMA) and acrylonitrile (AN). We assumed to obtain blends of varying miscibility, strongly disordering the PEO crystalline structure. We were interested also in the possibility of complexing Li^+ ions by C=O and C≡N groups and formation of mixed complexes with EO monomeric units, which could increase the mobility of charge carriers.

Three copolymers have been obtained containing 19, 36 and 55 mol. %, respectively, of AN monomeric units of an average molecular weight of ~13000 and polydispersity ~1.6. Five blends with PEO were obtained from each copolymer containing 10, 20, 30, 50 and 70 wt% of the copolymer, and then electrolytes were prepared containing 10 mol. % of LiClO_4 . The conductivities of thus obtained electrolytes are presented in Figs 7-9. It can be noticed that the highest ambient temperature conductivities were obtained for blends containing 10 wt% of the copolymers. The highest conductivity value of $7.3 \cdot 10^{-5}$ S/cm was obtained for the blend with a copolymer containing 36 mol. % of AN monomeric units. This electrolyte, however, exhibits good dimensional stability only up to 40°C. At elevated temperatures it is of advantage to generally use blends of a greater copolymer content. A number of them can work at above 100°C and exhibits then a conductivity of the order of $\sim 10^{-3}$ S/cm.

DSC and X-ray studies indicate that the introduction of copolymers very distinctly decrease the crystallinity, both for blends and electrolytes. In Fig. 10 is presented the magnitude of these effects for systems with a copolymer containing 36 mol. % of AN units. As can be noticed, a very clear synergistic effect occurs of LiClO_4 and the copolymer to disorder the electrolyte crystallinity and in electrolytes containing blends, 70-85 % of PEO occurs in the amorphous phase, while in electrolytes containing neat PEO ,

only 30 %. We did not observe a clear relationship between the ambient temperature conductivity and electrolyte crystallinity. Therefore, it seems that at a high amorphous phase content the conductivity depends to a greater extent on its conducting properties than on its content. DSC studies show that a majority of blends contain several amorphous phases of different T_g values, which indicates a limited miscibility in the amorphous phase. In the blends of copolymers containing 19 and 55 mol. % of AN monomeric units one phase had a glass transition temperature in the -50 - -63°C range, which indicates a very high PEO contents in these phases. The blends with a copolymer containing 36 mol. % of AN exhibit a distinctly better miscibility. On the basis of glass transition temperatures, from the Fox's equation it can be estimated that two phases are present containing ca. 60 and 30 wt% of PEO, respectively. Upon doping with LiClO₄ only one T_g value is observed, at -5, -7, +17 and +11°C at copolymer content 10, 30, 50 and 70 wt%, respectively.

In the electrolytes with the other copolymers one or two glass transition temperatures are observed. Their values are generally lower than those observed for systems with copolymers containing 36 mol. % of AN. Therefore, the high conductivity of blends containing 10 wt% of the latter copolymer cannot be explained by a larger elasticity of the amorphous phase. From DSC and X-ray studies it appears that also the amorphous phase content in these electrolytes is not greater than in the other systems. The higher polarity of this phase resulting from the presence of ester and nitrile groups may be the reason for the higher conductivity. FTIR studies rather excluded the possibility of mutual complexation of Li⁺ cations by EO monomeric units and C=O and C≡N groups. In the spectra of electrolytes, the ν C=O and ν C≡N bands remained practically unchanged. However, changes were observed characteristic for the formation of complexes by PEO. The most characteristic is the shift of the strong band of ν C-O-C vibrations from 1112 to 1092 cm⁻¹. The bands at 1360 and 1343 cm⁻¹ associated with CH₂ wagging motion in the crystalline phase are clearly weakened, and that at 1349 cm⁻¹ characteristic for the amorphous phase is increased.

The band at 1650 cm⁻¹ observed by some authors for blends with poly(methyl methacrylate) and attributed to the C=O--Li⁺ complexes results, in our opinion, from the presence of moisture in the sample studied.

Microscopic studies showed that in blends with a copolymer containing 36 mol. % of AN the amorphous phase is located outside the spherulites and in the other systems between the lamellas. It is very probable that the

intercrystalline amorphous phase assures better conditions for the ion transport than the intracrystalline phase.

Attempts have been made to increase the conductivity of blends by the addition of 20 wt% of propylene carbonate. The electrolytes thus obtained, however, are characterized by weak mechanical properties, and their conductivity at ambient temperature does not exceed $2 \cdot 10^{-4}$ S/cm and therefore further studies on these systems have been relinquished.

Theoretical work was also carried out on conductivity models in miscible and non-miscible blends. The results of this work are presented in a separate paper.

EXPERIMENTAL PART

1. Preparation of a gel based on poly(glycidyl methacrylate)

0.2g of LiClO₄ and 2.0g of propylene carbonate were introduced under nitrogen to a pressure reaction vessel. The reactor was heated until dissolution of the salt occurred. Then 0.3g of glycidyl methacrylate and 0.01g of dissolved benzoyl peroxide were introduced by means of a syringe. The polymerization was carried out at 70 °C for 3h. After that time, depending on the mode of crosslinking, ca. 0.3g of sulfur dioxide was added and the whole was heated at 50°C for 24h, or 0.1 wt% of a 20% BF₃ etherate solution in propylene carbonate. In this latter case a gel was obtained after 10 minutes. The other gels were obtained analogically.

2. Procedure for the preparation of gels based on lithium salts of maleic anhydride (MA) and styrene (St) copolymer semiesters

Method A

0.5g (0.0025 mol) of the MA/St copolymer was dissolved in 15 cm³ of DMSO. The solution obtained was added dropwise to an equimolar amount of a poly(ethylene glycol) allyl monoether alcoholate solution in 15 cm³ of DMSO, obtained from allyl ether and *n*-butyllithium. *n*-Butyllithium was used as a 1.4 molar solution in hexane.

To the obtained salt of the MA/St copolymer semiester was added 1 wt% (with respect to the salt) of a free radical initiator or photo initiator, and in the case of a gel of a mixed plasticizer composition, a determined amount of propylene carbonate. A thin layer of the solution was obtained, and the

excess of solvents was removed *in vacuo* at 60-90°C. The gel was obtained in the form of a film.

Method B

The solution of the lithium salt of the BM/St copolymer semiester obtained as described above was poured onto acidified water. The polymer precipitated was filtered off and purified by dissolution in acetone and precipitation by pouring onto water (three times). The polymer was dried *in vacuo* for 48h. 0.2g of the obtained acidic form of the MA/St copolymer semiester was dissolved in 3 cm³ of absolute methanol and converted into a salt by dropping in a equimolar amount (with respect to the carboxylic groups) of a *n*-butyl solution in hexane. Next, a required amount of DMSO and /or propylene carbonate and free radical initiator or photo initiator, a thin layer was poured out and methanol was removed. Gels were obtained by thermal crosslinking (at 70°C, ~1h), or photo thermally by means of UV radiation.

CONCLUSIONS

1. Polymeric blends comprising PEO and polar acrylic polymers do not permit the obtaining of electrolytes of ambient temperature conductivity exceeding 2·10⁻⁴ S/cm. They also do not form mechanically stable gels with plasticizers, which probably results from their linear structure and dissolution of the crystalline PEO phase.
2. Polymeric gels based on glycidyl methacrylate exhibit a conductivity similar to that of systems containing crosslinked PEO or copolymers of bi- and trifunctional acrylic monomers with EO monomeric units in the ester group. It seems of purpose to introduce to this type of matrices a certain amount of polar monomeric units such as that of acrylonitrile or acrylamide, which cause an increase in the polarity of the system and a small increase in the electrolyte conductivity. It seems, however, that the mode of gel preparation is of a lesser importance for the electrolyte conductivity and hence the radiation method, as a faster one, seems to be superior in comparison to chemical crosslinking.
- 3 Monoconducting gel electrolytes based on a maleic anhydride copolymer are a new and original system, which may find application due to the low cost of the starting materials. Although the procedure is far from being optimized, the initial conductivity values of the order of 7·10⁻⁴ S/cm at 20°C

and $2 \cdot 10^{-5}$ S/cm at -55°C seem to be promising and we believe that during further studies attention should be concentrated on these systems, also on the possibility of using them as matrices in electrolytes containing inorganic lithium salts.

REFERENCES

1. D. Davous, B. Sebille, *Europ. Polym. J.* **16**, 347 (1980)
2. K. M. Abraham, M. Alamgir, *J. Electrochem. Soc.* **137**, 1657 (1990)
3. H. Hong, Ch. Liquan, H. Hoejie, X. Rongjian, *Electrochimica Acta*, **37**, 1671
4. J. S. Lundsquad, S. Yde-Andersen, R. Kokslang, D. R. Shackle, R. A. Austinin, D. Fauteux, Proc. II Int. Symposium on Polymeric Electrolytes, Siena 1989, B. Scrosati Ed. Elsevier Applied Science, London, New York, 1990 p.395
5. R. Huq, R. Kokslang, P.e. Tonder, G. C. Farrington, *Electrochimica Acta* **37**, 1681 (1992); *Solid State Ionics* **57**,277 (1992)
6. P. S. Prasad, B. B. Owens, W. H. Smyrl, A. Selvaggi and B. scrosati in "Resent Advances in Fast Ion conducting Materials and Devices", B. V. R. Chowdari, Q. G. Liu and L. Q. Chen Eds. World Scientific, Singapoore 1990 p. 170
7. H. Ba, X. Peng, Y. Qi, D. Chen, F. Wang, *Makromol. Chem.* **191**, 2529 (1990)
8. J. Prud'homme, M. Gauthier, P. E. Harvey, *Macromolecules* **25**, 6480 (1992)
9. F. M. Gray "Solid Polymer Electrolytes - Fundamentals and Technological Applications" VCH Weinheim FRG 1991, Chapter 6
10. W. Krawiec "Linear and Comb-like Copolymers of Maleic Anhydride Terpolymers" Ph. D. Thesis, Warsaw University of Technology, 1991
11. Z. Florjańczyk, W. Krawiec, T. Listoś, W. Wieczorek, J. Przyłuski, Proc. VII Int Conference on Solid State Ionics, Hakone, 1989, S. Hoshino, T. Takahashi Eds. p.188
12. K. Such "Polymer Blend Electrolytes", Ph. D. Thesis, Warsaw University of Technology, 1990
13. Z. Florjańczyk, K. Such, M. Wasiucionek, *Polymer* **32**, 3422 (1991)
14. Z. Florjańczyk, K. Such, W. Wieczorek, *J. Macromol. Sci. Pure and Appl. Chem.* **A-29**,10 (1992)
15. W. Wieczorek, K. Such, Z. Florjańczyk, J. Przyłuski, *Electrochimica Acta* **37**, 1565 (1992)

Table 1. Conductivity of gels based on glycidyl methacrylate and crosslinked with sulfur dioxide

No.	Polymer	PC content	LiClO ₄ concentration [wt%]	Conductivity [S/cm]	
		[wt%]		298K	323K
1	Poly(glycidyl methacrylate)	60	8	1.8·10 ⁻⁴	3.0·10 ⁻⁴
2		70	8	2.6·10 ⁻⁴	7.4·10 ⁻⁴
3		80	8	1.6·10 ⁻³	3.9·10 ⁻³
4		80	6	1.3·10 ⁻³	2.7·10 ⁻³
5		80	5	5.8·10 ⁻⁴	1.4·10 ⁻³
6		80	4	3.5·10 ⁻⁵	6.3·10 ⁻⁵
7		80	8 ^a	3.1·10 ⁻⁴	5.4·10 ⁻⁴
8		80 ^b	8	1.7·10 ⁻³	2.5·10 ⁻³
9		70 ^c	8	6.3·10 ⁻⁵	1.3·10 ⁻⁴
10	Poly(glycidyl methacrylate- -co-methyl acrylate) ^d	80	8	1.8·10 ⁻³	3.4·10 ⁻³
11	Poly(glycidyl methacrylate- -co-acrylamide) ^d	80	8	3.3·10 ⁻³	5.7·10 ⁻³
12	Poly(glycidyl methacrylate- -co-acrylonitrile) ^d	80	8	3.8·10 ⁻³	7.6·10 ⁻³
13	Poly(glycidyl methacrylate- -co-styrene) ^d	80	8	no gel	was formed

a CF₃SO₃Li was used as the salt

b Plasticizer: propylene sulfite

c Plasticizer: 3-chloropropylene sulfite

d Comonomers mole ratio = 1:1

Table 2. Conductivity of gels based on glycidyl methacrylate (GMA) copolymers with monomers A of various polarity^a.

Comonomer A	GMA contribution in copolymer	<u>Conductivity</u> [S/cm]	
		298K	323K
	[mol. %]		
Methyl acrylate	50	$2.0 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$
Butyl acrylate	50	$2.2 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$
Methyl methacrylate	30	$2.1 \cdot 10^{-3}$	$5.1 \cdot 10^{-3}$
Acrylamide	50	$3.5 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$
Acrylonitrile	50	$2.2 \cdot 10^{-3}$	$3.5 \cdot 10^{-3}$
Styrene	60	$1.8 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$
Poly(ethylene glycol)	55	$1.9 \cdot 10^{-3}$	$3.4 \cdot 10^{-3}$
diglycidyl ether			

^a LiClO₄: 8 wt%; propylene carbonate (PC): 80%; crosslinking agent: BF₃ etherate (0.1 wt%) (20 % solution in PC)

Table 3. Conductivity and TGA results of gels based on glycidyl methacrylate copolymers with butyl acrylate^a

Plasticizer	Plasticizer contribution [wt%]	Conductivity		[S/cm]	Mass loss in 323K	60	100	wt% at: 150°C
		298K	72					
Propylene carbonate			$1.8 \cdot 10^{-4}$	$4.3 \cdot 10^{-4}$	1.1	6.9	23.0	
Propylene carbonate	80		$2.2 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$				
Propylene carbonate/ propylene sulfite (1:1)	72		$5.3 \cdot 10^{-4}$	$1.4 \cdot 10^{-3}$	1.2	7.2	25.3	
Propylene carbonate/ ethylene carbonate (1:1)	70		$4.8 \cdot 10^{-4}$	$1.1 \cdot 10^{-3}$	1.2	7.2	27.7	
Propylene carbonate/ ethylene carbonate (1:1)	70 ^b		$3.6 \cdot 10^{-4}$	$7.4 \cdot 10^{-4}$	0.8	5.3	20.3	

^a The gels were doped with 8 wt% of LiClO₄; BF₃·(C₂H₅)₂O was used as the crosslinking agent
^b CF₃SO₃Li was used as the salt

Table 4

System ^a	Sample	x	y	DMSO wt%	PC wt%	Li/Polymer wt%	Conductivity [S/cm]	
							r.t.	~50 °C
I	A	2				2.13	9.63·10 ⁻⁸	2.21·10 ⁻⁷
	B	16				0.73	8.44·10 ⁻⁸	1.94·10 ⁻⁶
	C	16		20			6.63·10 ⁻⁵	1.67·10 ⁻⁴
	D	45				0.32	2.45·10 ⁻⁹	4.63·10 ⁻⁹
II	A	2				2.01	1.47·10 ⁻⁶	4.02·10 ⁻⁶
	B	2					6.98·10 ⁻⁴	1.32·10 ⁻³
	C	16		19	64		5.21·10 ⁻⁷	1.22·10 ⁻⁶
	D	45				0.34	5.33·10 ⁻⁹	1.05·10 ⁻⁸
III	A	3		10		1.76	1.01·10 ⁻⁴	2.04·10 ⁻⁴
	B	3		14		1.76	1.49·10 ⁻⁴	2.85·10 ⁻⁴
	C	3		17		1.76	2.38·10 ⁻⁴	1.04·10 ⁻³
	D	3		20	20	1.76	7.68·10 ⁻⁴	1.88·10 ⁻³
	E	6				1.32	2.15·10 ⁻⁵	8.12·10 ⁻⁵
	F	6		24		1.32	4.76·10 ⁻⁵	7.84·10 ⁻⁵
	G	6		28		1.32	6.11·10 ⁻⁵	1.25·10 ⁻⁴
	H	9		20		1.06	7.28·10 ⁻⁶	3.98·10 ⁻⁵
	J	9		27		1.06	2.70·10 ⁻⁵	1.06·10 ⁻⁴

^a for the description of systems I, II and III see the bimonthly report of January 4, 1993

Table 5. VTF parameters for some electrolytes based on maleic anhydride /styrene copolymer

Sample	A [S·K ^{0.5} ·cm ⁻¹]	E [K]	T ₀ [K]
I A	4.6·10 ⁻⁴	998	120
I B	1.3·10 ⁻³	179	277
I C	4.9	173	95
I D	2.1·10 ⁻³	175	296
III A	2.6	1280	257
III C	36.3	1450	132
III D	1.3	538	180
III E	5.2·10 ⁻²	357	224
III H	7.6·10 ⁻²	354	248
III J	1·10 ⁻²	120	257

Table 6. Thermogravimetric studies of polymeric electrolytes

Sample	Mass loss in wt% at:				
	50	70	100	150	200°C
III B	1.1	2.5	4.6	9.4	13.7
III C	2.4	7.2	13.2	18.0	21.6
III D	1.2	2.5	4.0	4.5	13.0

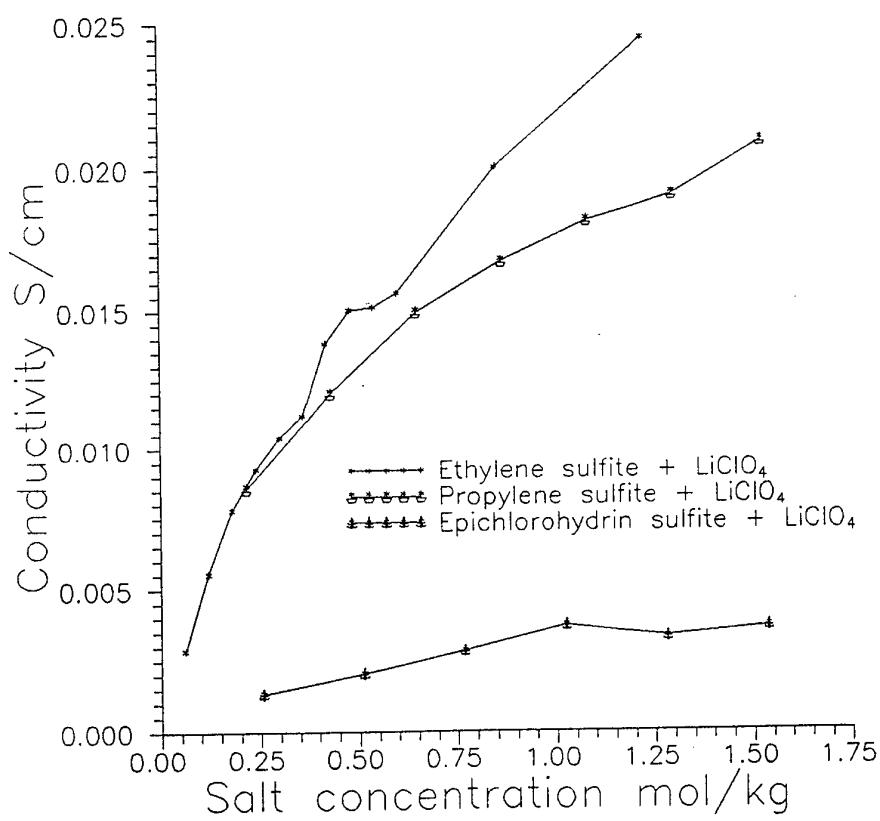


Fig.1. LiClO_4 conductivity in ethylene sulfite, propylene sulfite and 3-chloropropylene sulfite vs salt concentration at 20°C

FIGURE 2

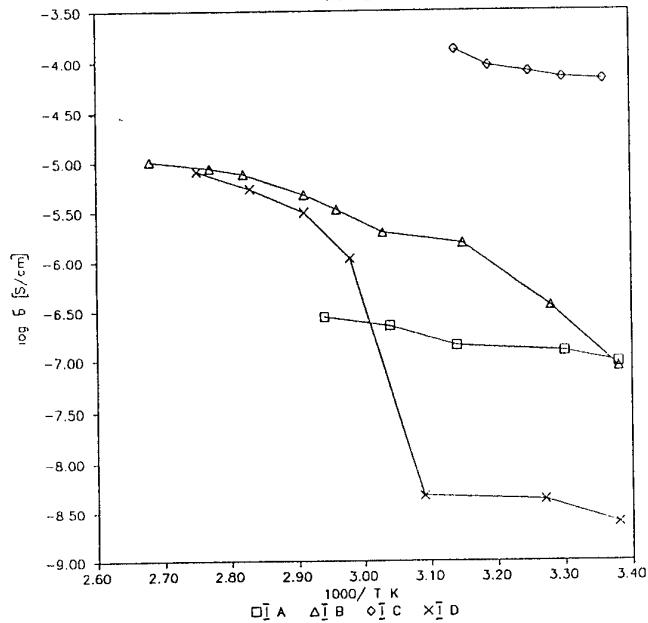


FIGURE 3

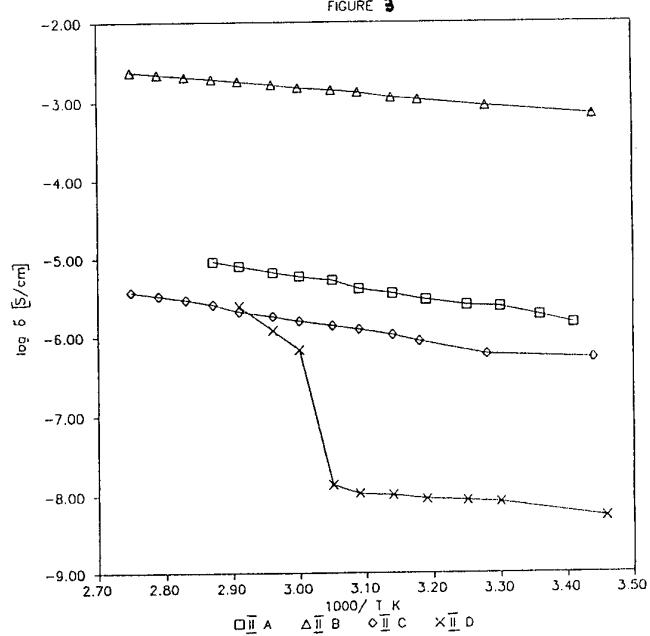


FIGURE 4

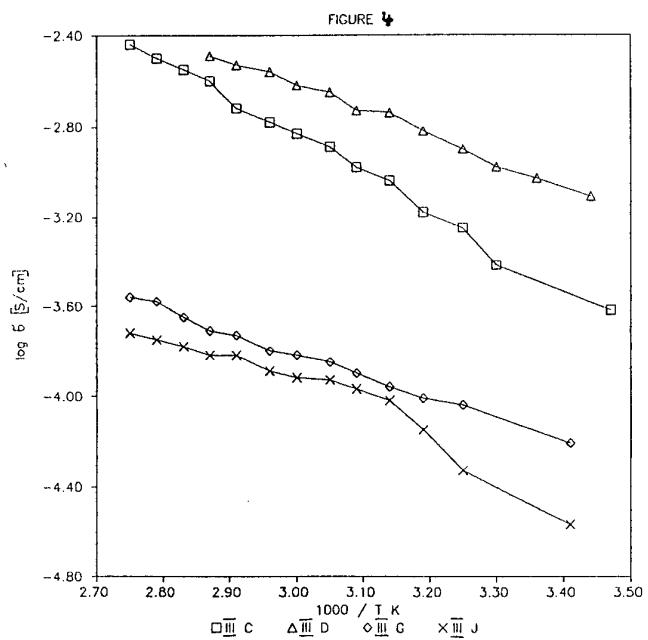
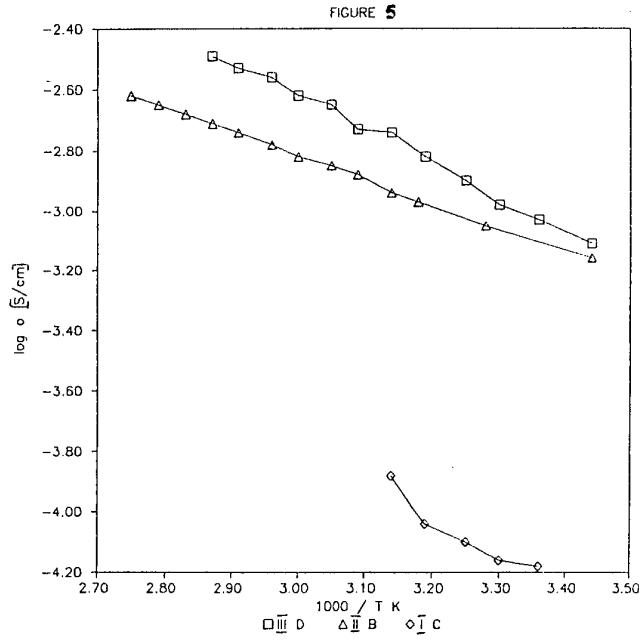


FIGURE 5



Figs 2-5. Conductivity of electrolytes based on salts of maleic anhydride and styrene copolymer semiesters vs temperature

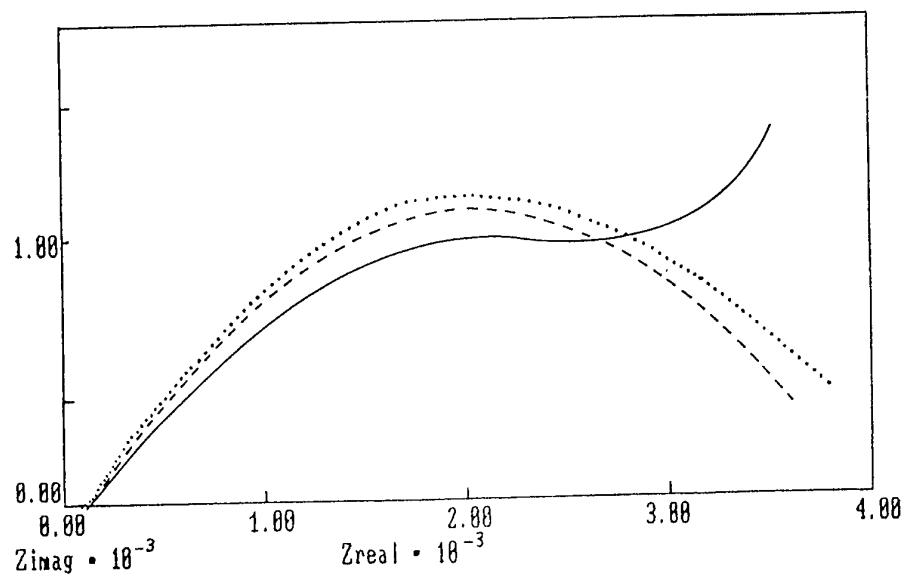


Fig. 6. Impedance diagram for a symmetrical Li PGE Li cell at 40°C

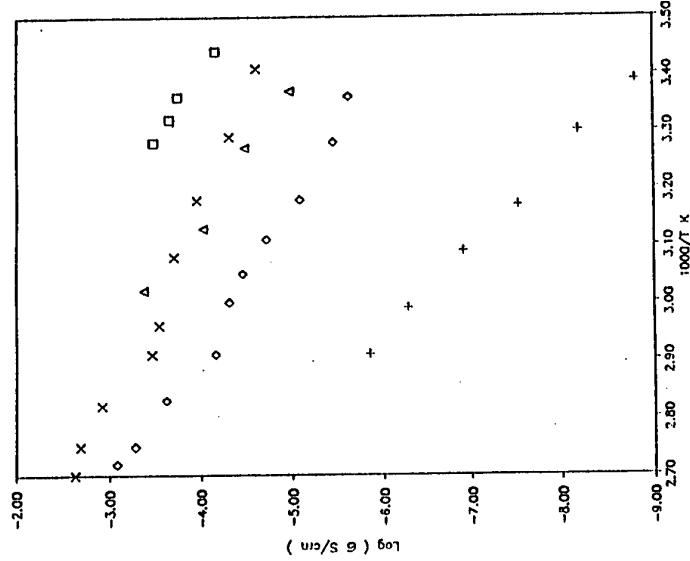


Fig. 7

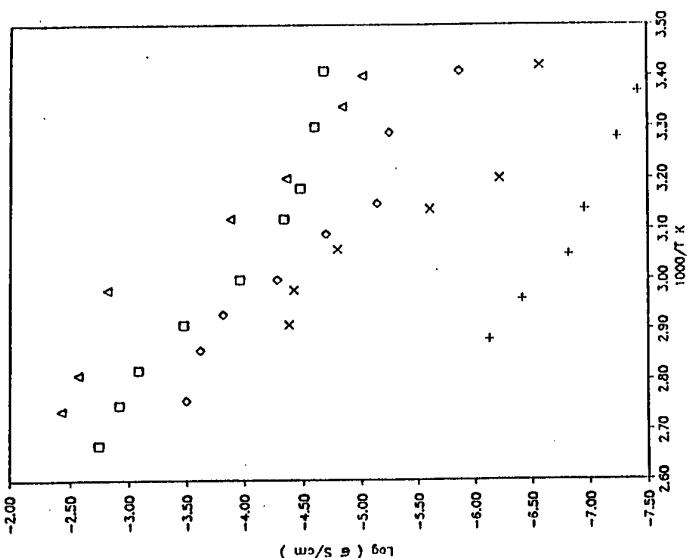


Fig. 8

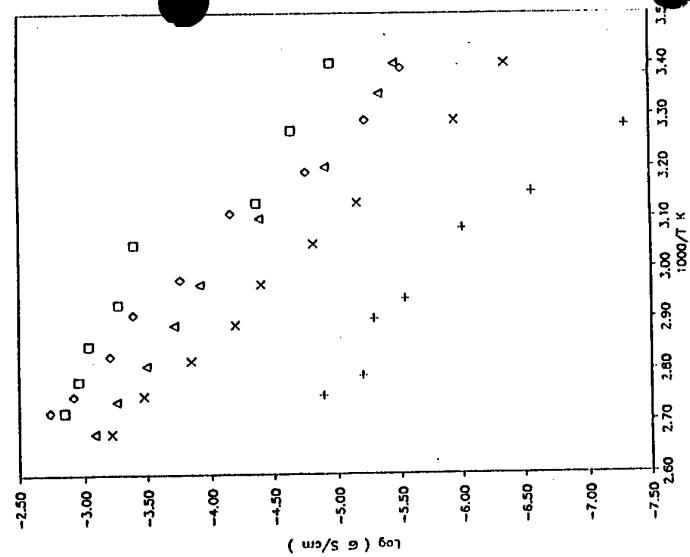


Fig. 9

Fig. 7-9. Conductivity of PEO blends with acrylonitrile (AN)/methyl methacrylate (MMA) copolymer (containing 36 mol. % of AN - Fig. 7; 55 mol. % of AN - Fig. 8; 19 mol. % of AN - Fig. 9), doped with 10 mol. % of LiClO₄ vs temperature for different blend compositions: [□] - PEO/copolymer = 9:1; [x] - 5:5; [Δ] - 8:2; [+] - 3:7; [◊] - 7:3

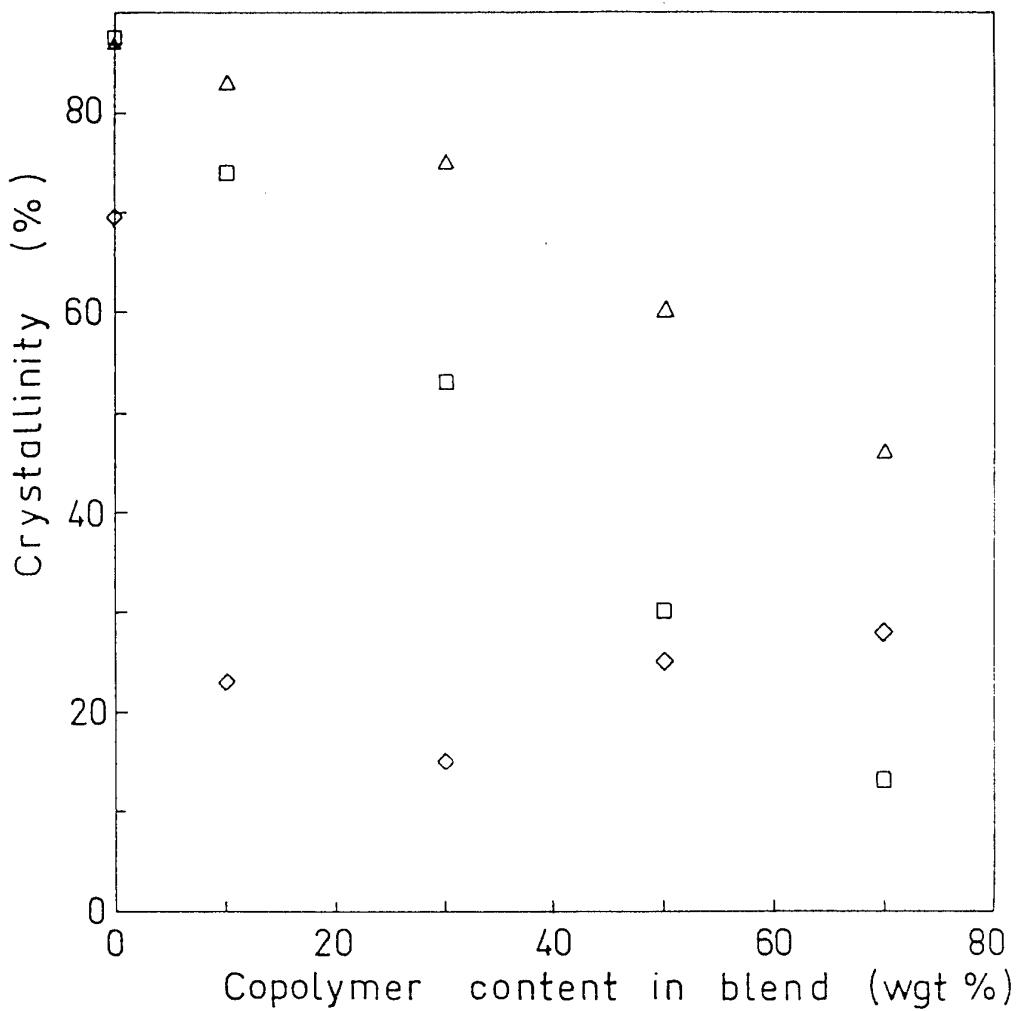


Fig.10. Degree of crystallinity vs concentration of the added AN-co-MMA or PEO-(AN-co-MMA) blends. [□] - degree of the undoped blend crystallinity; [△] - degree of crystallinity calculated in respect to PEO concentration in the blend; [◊] - degree of crystallinity of the PEO-(AN-co-MMA) blends doped with 10 mol. % of LiClO₄ calculated in respect to PEO concentration in the blend.